Synergistic Interactions in Electrochemical Water Splitting

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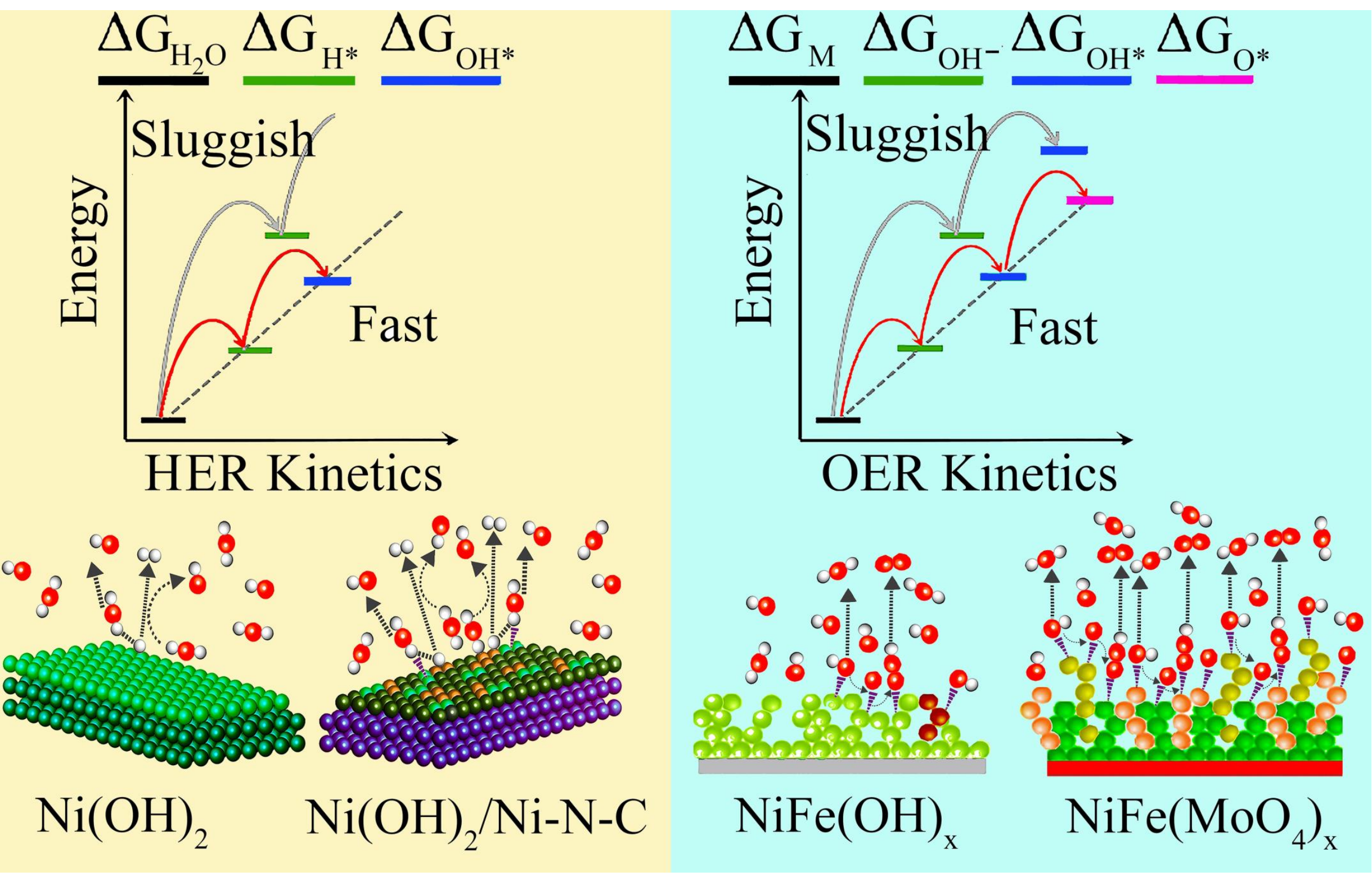
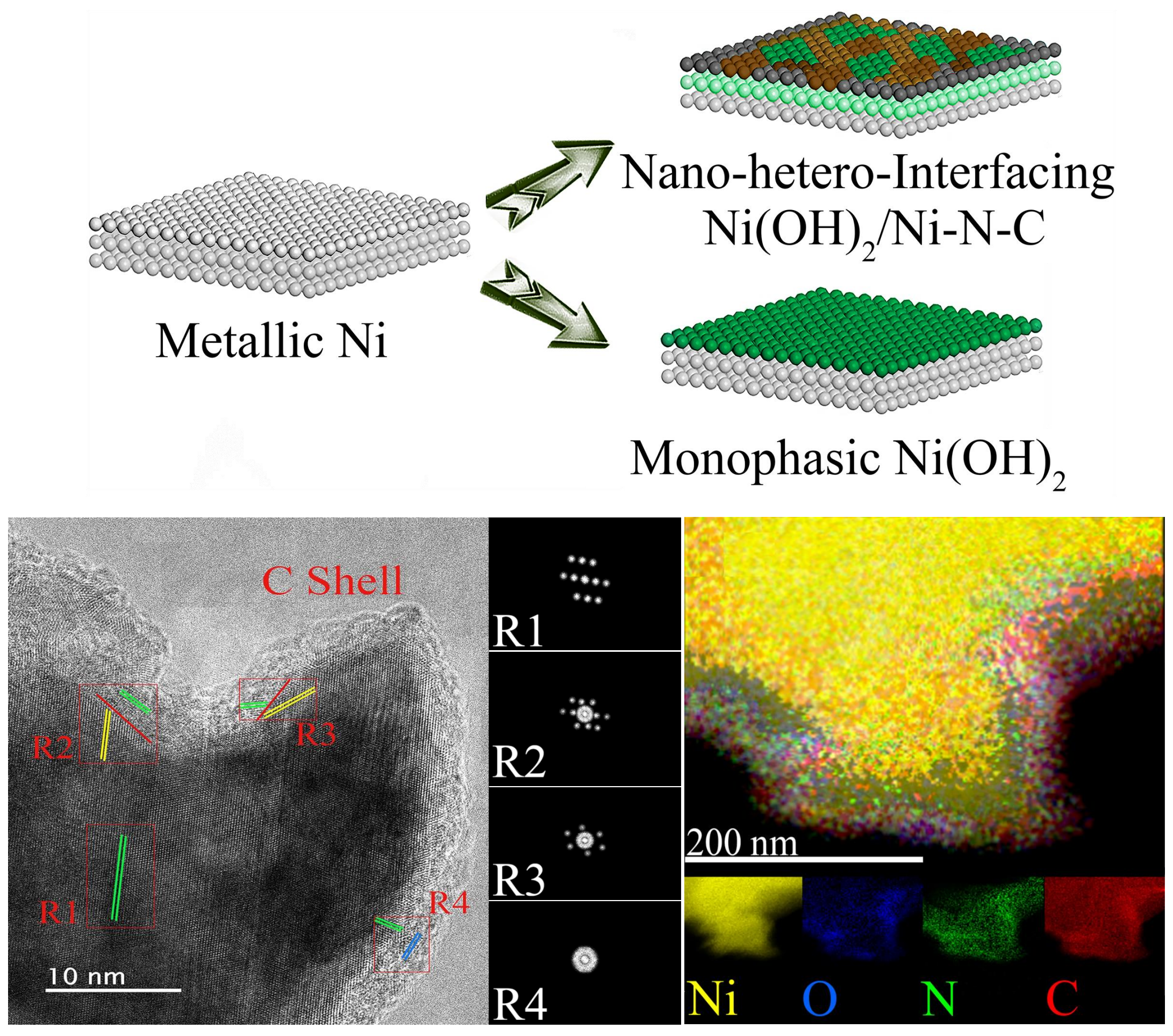
Introduction



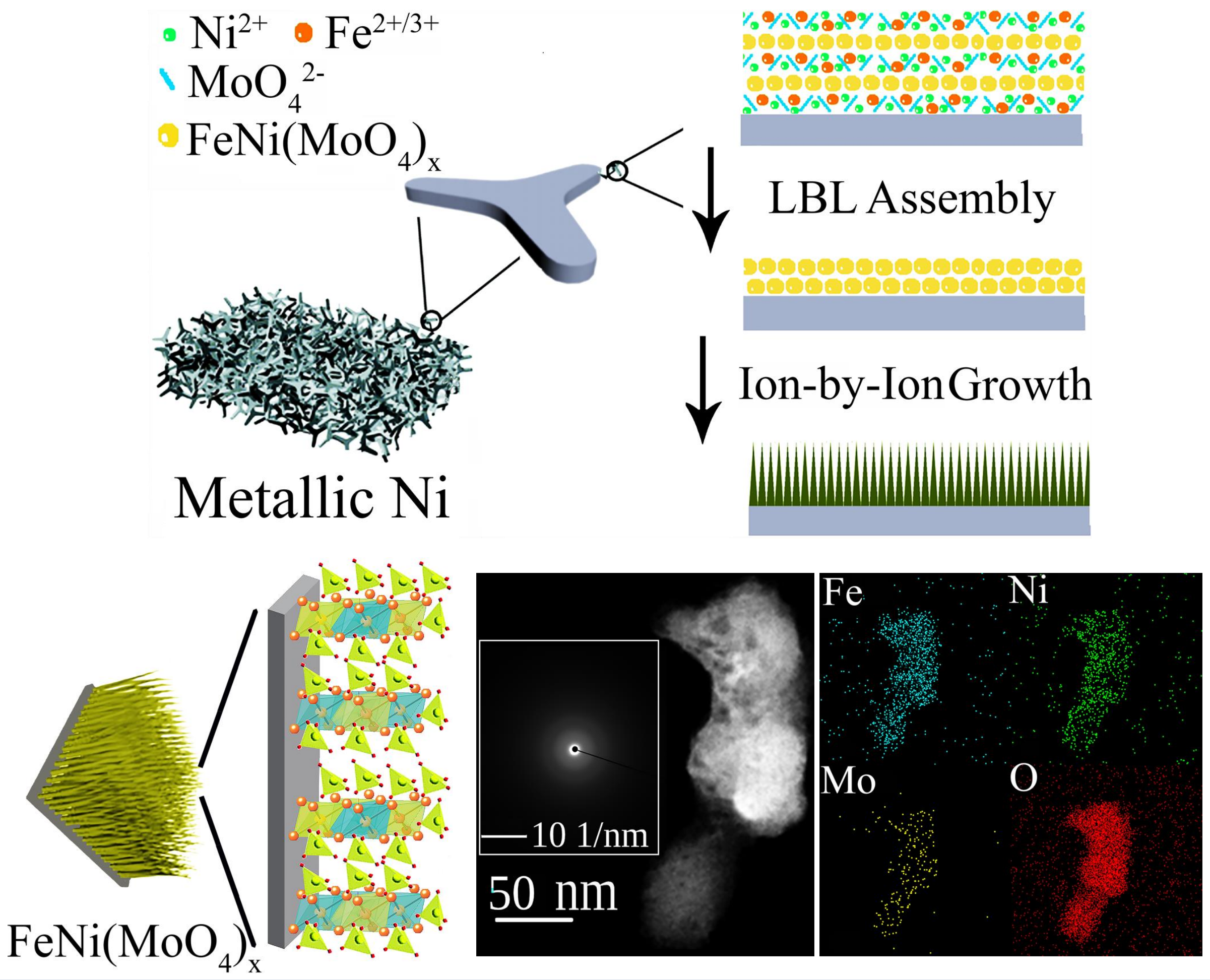
Developing efficient noble metal-free electrocatalysts for water electrolysis requires understanding of activity enhancement factors. Electrocatalytic synergy is a functional yet underrated concept in catalyst development. Often, it materializes as intermetallic interaction between different metals. Ensemble effects brought by synergistic interactions between two or more structural entities on Faradaic electron transfer process can be induced by cumulative surface-active sites, interfacial charge transfer, and modulating electronic structure[1]. So far, electrocatalytic synergy has been mainly studied for metal dopants[2] and host-guest atomic interactions in heterostructures[3].

We demonstrate both intermetallic and interphasic synergy to enhance the intrinsic electrocatalytic activity for oxygen evolution reaction (OER) and hydrogen evolution reaction (HER). Cosynergistic molybdate oxo-anionic modification of a FeNi-model catalyst and interphasic nano-hetero-interfacing of $Ni(OH)_2$ and Ni-Ni-C structures are reported to boost OER and HER performances, respectively in alkaline media.

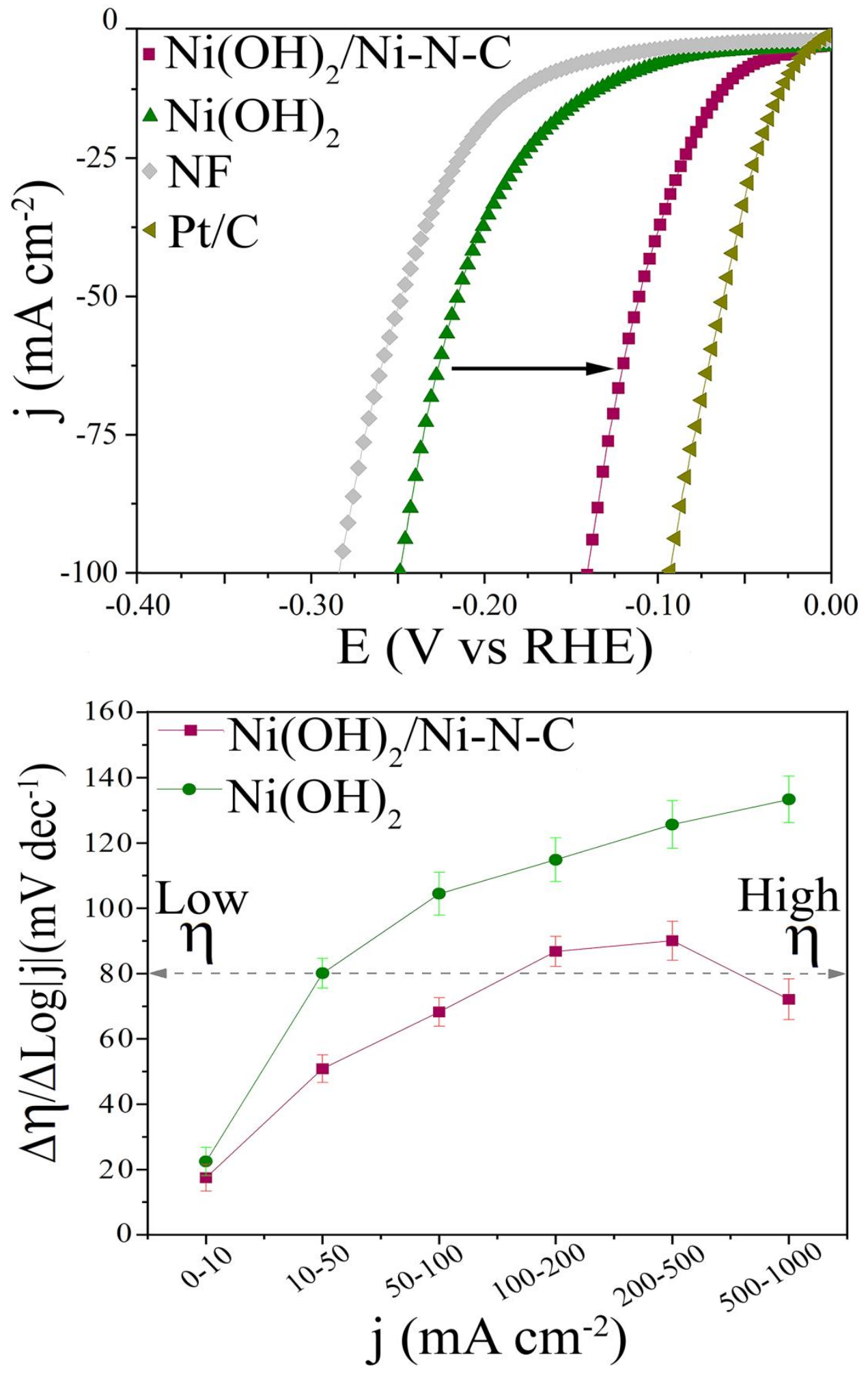
Forging Interphasic & Intermetallic Synergy in Catalysts



- ☐ Regulation of short-range ordered $Ni(OH)_2$ and Ni-N-C phases on metallic Ni
- ☐ Nano-hetero-interfacing of $Ni(OH)_2$ and Ni-N-C phases induces induce interphasic
- ☐ Layer-by-layer (LBL) assembly & ion-by-ion growth of $FeNiMoO_4$ on metallic Ni
- ☐ Surface modification of FeNi oxide with molybdate oxo-anions induces intermetallic synergy



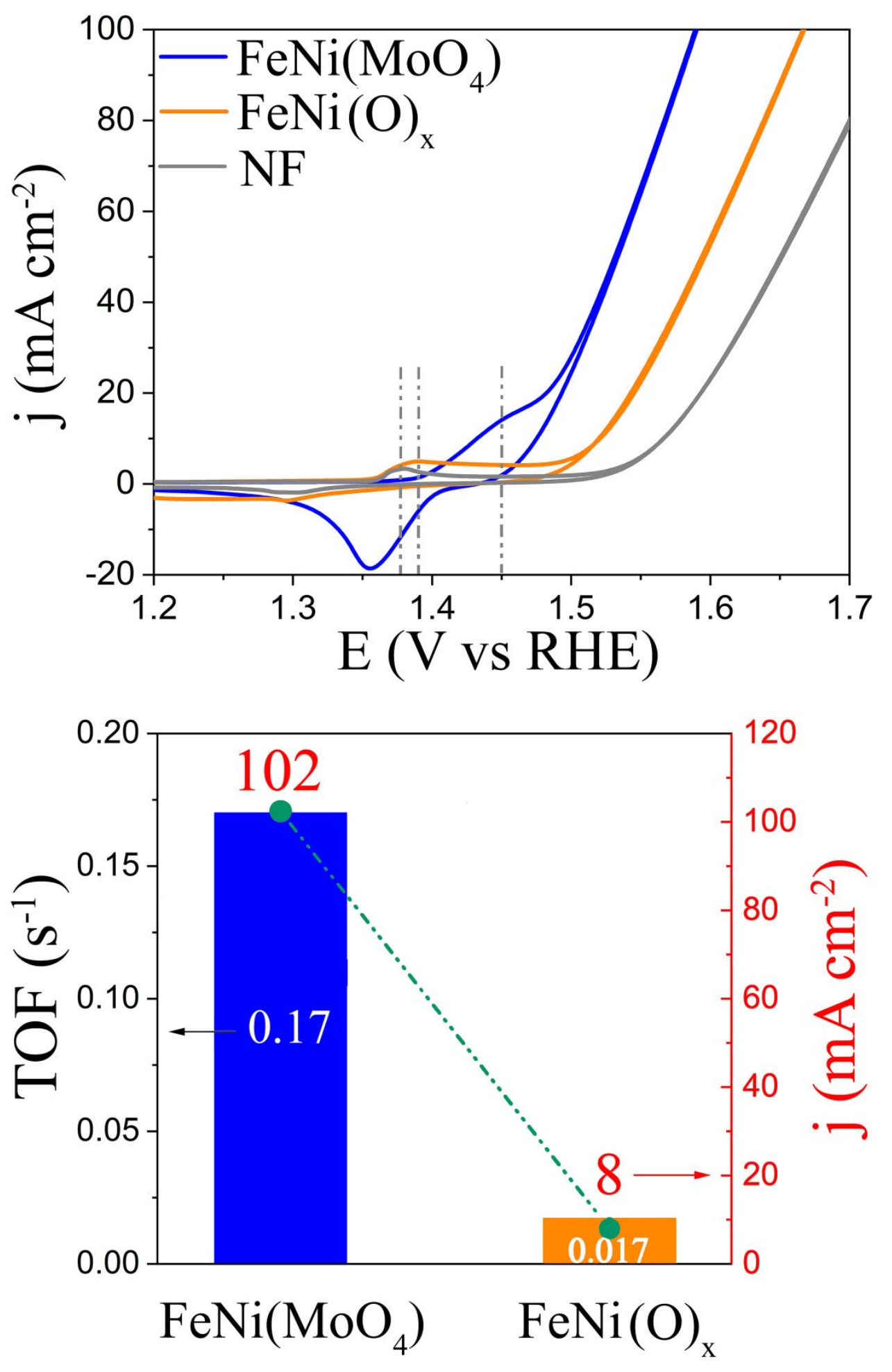
HER



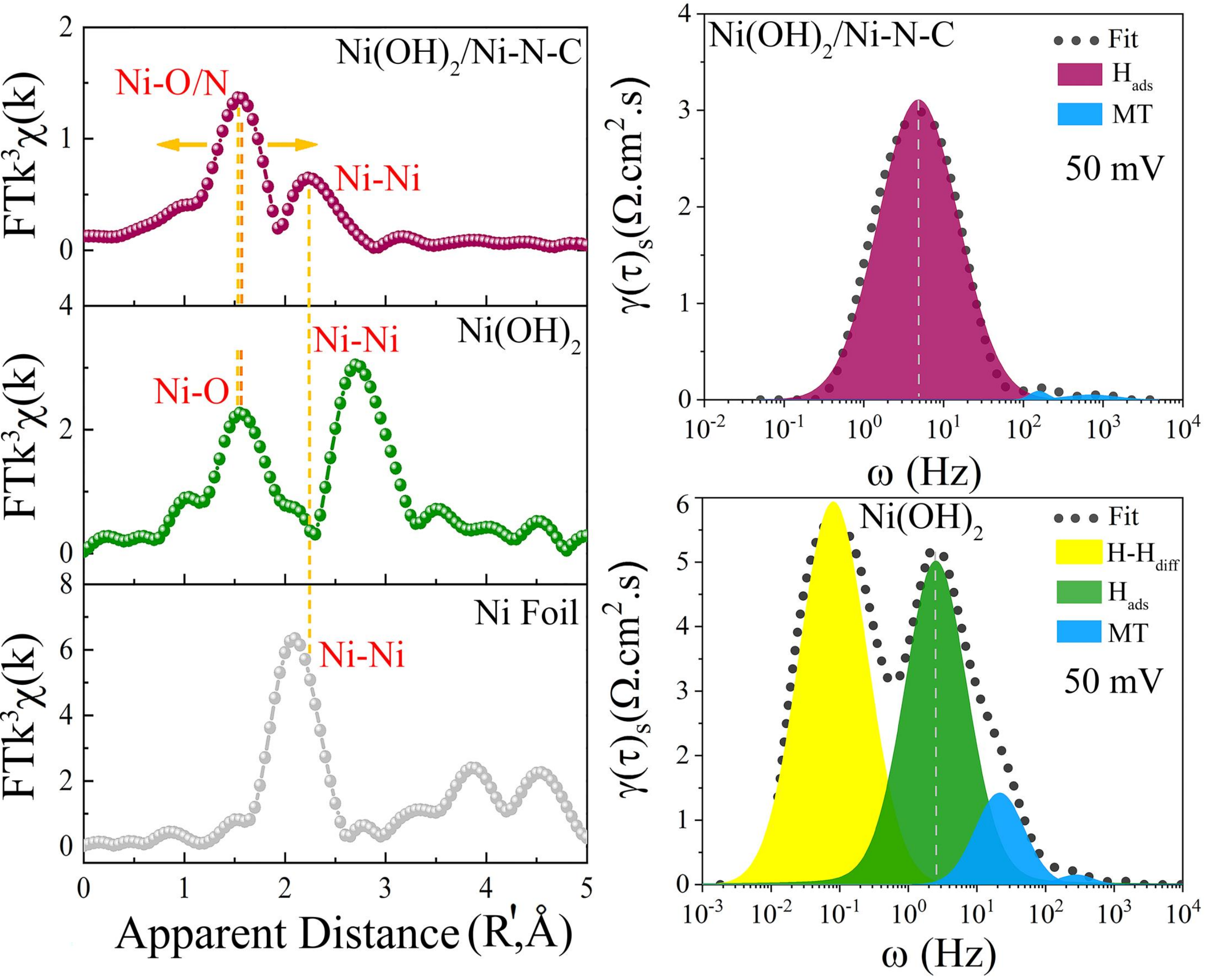
Electrocatalytic Performance

- ☐ $Ni(OH)_2$: good water dissociation promoter, weak H desorption, Ni-N-C: good OH adsorption, weak water dissociation
- ☐ Interphasic synergy formed by local nano-hetero-interfaces of $Ni(OH)_2$ and Ni-N-C boosts intrinsic HER performance
- ☐ Fe & Ni don't have optimal adsorption intermediate as monometallic active sites
- ☐ Intermetallic synergy between MoO_4 oxo-anions & Fe/Ni active sites boosts intrinsic OER performance

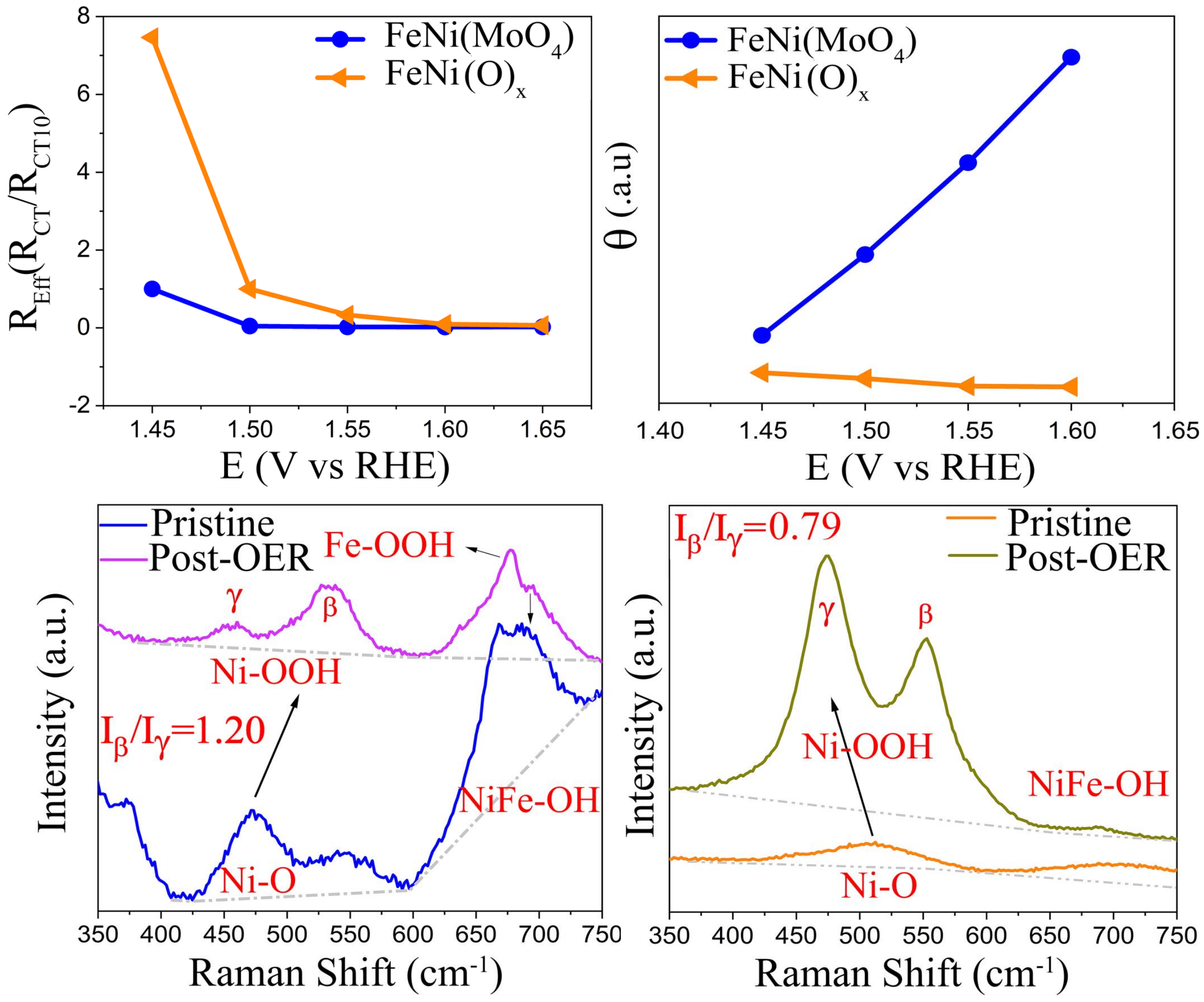
OER



Mechanistic Analysis



- ☐ Nano-hetero-interfacing alters Ni coordination by inducing metallicity & enhanced electron density
- ☐ Ni active sites have low charge transfer resistance over $Ni(OH)_2$/Ni-N-C, while monophasic $Ni(OH)_2$ faces a large resistance to H_2 recombination
- ☐ Molybdate modification minimizes interfacial charge transfer & enhances intermediate adsorption over Fe and Ni active sites
- ☐ Molybdate modification induces phase transformation to β-NiOOH & γ-FeOOH



Conclusion

- Different forms of synergistic interactions exist to promote water splitting.
- Intermetallic synergy between different metal atoms & interphasic synergy between different phases in monometallic structures significantly impact OER & HER reactions.
- Synergistic interactions alter metallic coordination environment & induce phase transformation during electrocatalysis.
- Enhancing interfacial charge transfer & reducing the contributing resistances could be resulted by synergistic effects

Reference & Acknowledgement

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3. Dastafkan, K. Wang, W. Meyer, Q. Li, Y. Zhang, Q. Zhao, C. *Adv. Funct. Mater.* 2021, 32, 2107342.

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